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Crystal Growth of Superconducting La2126 without HIP Treatment

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Abstract. We have succeeded in the crystal growth of the superconducting $\text{La}_{2-x-y}\text{Ba}_x\text{Sr}_y\text{CaCu}_2\text{O}_6$ of the La2126 phase by only the traveling-solvent floating-zone (TSFZ) method without the hot-isostatic-pressure (HIP) treatment. In the TSFZ growth, we added a small amount of B_2O_3 to the solvent for the stabilization of the growth and used high-pressure oxygen of ~ 10 atm as a growth atmosphere for the suppression of oxygen defects. We have obtained single crystals with the size of the order of $2 \times 2 \times 3 \text{ mm}^3$ and determined the composition to be $\text{La}_{1.80}\text{Ba}_{0.07}\text{Sr}_{0.19}\text{Ca}_{0.97}\text{Cu}_{1.97}\text{O}_6$ by the inductively-coupled-plasma atomic-emission-spectrometry. The powder x-ray diffraction has revealed that the crystals are of the single phase of La2126 and include no impurity phases such as $\text{La}_{2-x}\text{M}_x\text{CuO}_4$ (M: alkaline earth). The as-grown single crystals have shown superconductivity of the bulk with the transition temperature $T_c = 20 \text{ K}$.

Keywords: superconductivity, cuprate, La2126, crystal growth, traveling-solvent floating-zone method

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The compound $\text{La}_{2-x}\text{M}_x\text{CaCu}_2\text{O}_6$ (M: alkaline earth) of the so-called La2126 phase has a pair of pyramidal Cu-O planes in the unit cell, which is the only electrically active part [1]. Because of the simple crystal structure, La2126 is expected to be a suitable system to extract the important information about the electronic state in the Cu-O plane.

As for single crystals of the superconducting La2126, the hot-isostatic-pressure (HIP) treatment, namely, post-annealing of obtained single-crystals above 1000°C under an oxygen pressure of ~ 300 atm is inevitable [2]. Therefore, we have aimed to obtain large-sized single crystals of the superconducting La2126 by only the traveling-solvent floating-zone (TSFZ) method without the HIP treatment.

Feed rods for the TSFZ growth were prepared by the solid-state reaction. High-purity powders of La_2O_3 , BaCO_3 , SrCO_3 , CaCO_3 and CuO were mixed and sintered. After cycles of grinding and calcining in air at 900 – 1050°C for 24 h, the powder mixtures were isostatically cold-pressed into a rod of 6 mm in diameter and ~ 100 mm in length and sintered in air at 1130 – 1150°C for 36 h. A solvent rod was also prepared by solid-state reaction using high-purity powders of La_2O_3 , MCO_3 , CaCO_3 and CuO in the molar ratio of La : M : Ca : Cu = $2-x$: x : 1 : 4. The powders were mixed and sintered in air at 900°C for 12 h. After pulverization, the powder mixtures were isostatically cold-pressed into a rod of 6 mm in diameter. The rod was sintered in air at 900°C for 12 h. The sintered rod was sliced into pieces and a piece of ~ 0.4 g was used as a solvent for the TSFZ growth. The TSFZ growth was performed under

an oxygen pressure of ~ 10 atm in an infrared heating furnace. The growth speed was 0.5 mm/h. Crystals thus obtained were evaluated by the powder x-ray diffraction and the x-ray back-Laue photography. The composition was analyzed by the inductively-coupled-plasma atomic-emission-spectrometry (ICP-AES). The magnetic susceptibility, χ , was measured using a SQUID magnetometer. The in-plane electrical resistivity, ρ_{ab} , was measured by the dc four-point probe method.

Table 1 displays the compositions of feed rods and obtained single-crystals analyzed by ICP-AES, lattice parameters, the superconducting transition temperature, T_c , and the superconducting volume fraction (SVF) estimated from χ at 2 K on zero-field cooling. First, the crystal growth using the Feed Rod I free of Ba and Sr was attempted. The growth was sufficiently stable that a crystal rod consisting of a lot of single crystals has been obtained. The size of one crystal (Crystal I) is the order of $1 \times 1 \times 2 \text{ mm}^3$. The x-ray measurements have revealed that the Crystal I is a single crystal of the La2126 phase. The Crystal I has shown superconductivity with $T_c = 18 \text{ K}$, but SVF is as small as $\sim 0.5\%$. The small SVF may be due to oxygen defects.

Since ionic radii of Ba^{2+} or Sr^{2+} are larger than that of Ca^{2+} , it is expected that the substitution of Ba or Sr for Ca increases the lattice parameters so that oxygen is introduced into the crystal enough for the appearance of superconductivity with a large SVF. Then, the crystal growth using the Feed Rod II with Ba and Sr was tried. Although the growth was not so stable, a crystal rod made up of plenty of single crystals has been obtained. The size of one crystal (Crystal II) is also the order

TABLE 1. Compositions of feed rods and obtained single-crystals analyzed by ICP-AES, lattice parameters a and c , T_c , and the superconducting volume fraction (SVF) for the La2126 crystals growth by the TSFZ method. T_c is defined as the onset temperature of the Meissner effect. SVF is estimated from χ at 2 K on zero-field cooling.

	La	Ba	Sr	Ca	Cu	a (Å)	c (Å)	T_c (K)	SVF (%)
Feed Rod I (Nominal)	1.7	-	-	1.3	2				
Crystal I (ICP)	1.89	-	-	1.20	1.91	3.823	19.41	18	~ 0.5
Feed Rod II (Nominal)	1.7	0.1	0.2	1	2				
Crystal II (ICP)	1.78	0.07	0.19	1.13	1.83	3.832	19.58	30	~ 1
Feed Rod III (Nominal)	1.7	0.1	0.2	1	2.2				
Crystal III (ICP)	1.80	0.07	0.19	0.97	1.97	3.827	19.54	20	~ 40

of $1 \times 1 \times 2 \text{ mm}^3$. It has been revealed that the Crystal II is a single crystal of the La2126 phase and exhibits superconductivity with $T_c = 30 \text{ K}$, but SVF is as small as that in the Crystal I. When SVF is very small, a suspicion comes up that the superconductivity is not due to the La2126 phase but due to a small amount of impurity phases such as $\text{La}_{2-x}\text{M}_x\text{CuO}_4$ of the so-called La214 phase. However, no impurity phases have been detected in the Crystal I nor in the Crystal II by the x-ray diffraction. From the composition analysis by ICP-AES, it has turned out that the Crystal II is short of Cu, which is guessed to be caused by the evaporation of Cu out of the molten zone in the TSFZ growth. Therefore, the small SVF may be due to defects of Cu.

Then, the crystal growth using the Feed Rod III with an excess Cu was tried. Here, 2 wt.% of B_2O_3 was added to the solvent so as to increase the viscosity of the solvent and stabilize the growth. The growth was sufficiently stable that a crystal rod consisting of many single-crystals has been obtained. The size of one crystal (Crystal III) is as large as the order of $2 \times 2 \times 3 \text{ mm}^3$. The x-ray back-Laue photograph of the (001) plane has confirmed the single crystallinity as shown in Fig. 1, and the powder x-ray diffraction has revealed that the Crystal III is of the single phase of La2126 and includes no impurity phases such as $\text{La}_{2-x}\text{M}_x\text{CuO}_4$. The composition of the Crystal III has been determined to be $\text{La}_{1.80}\text{Ba}_{0.07}\text{Sr}_{0.19}\text{Ca}_{0.97}\text{Cu}_{1.97}\text{O}_6$ by ICP-AES. The Crystal III has shown superconductivity with $T_c = 20 \text{ K}$ and a large SVF, as shown in Fig. 2. These results can claim that the superconductivity is of the bulk of the La2126 phase. However, the superconducting transition is quite broad. The inhomogeneous distribution of cations and oxygen in the crystal may induce the inhomogeneity of the hole concentration, leading to the broad transition.

In conclusion, it is effective for obtaining the superconducting La2126 crystals with a large SVF by only the TSFZ method without the HIP treatment to increase the lattice parameters by doping Ba and Sr and to lessen the defects of Cu. However, it will be necessary for the observation of a sharp superconducting transition to make the distribution of cations and oxygen in the crystal ho-

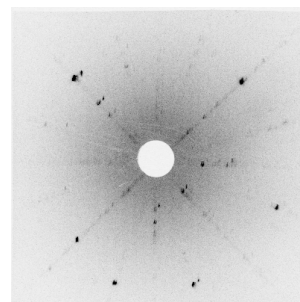


FIGURE 1. X-ray back-Laue photograph of the (001) plane of the single-crystal $\text{La}_{1.80}\text{Ba}_{0.07}\text{Sr}_{0.19}\text{Ca}_{0.97}\text{Cu}_{1.97}\text{O}_6$.

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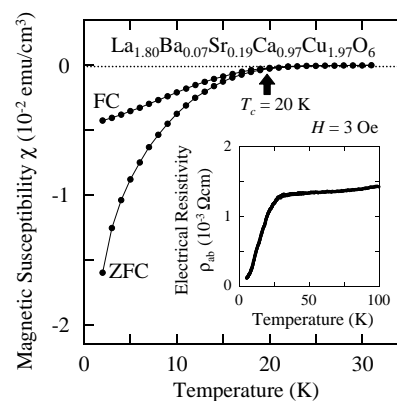


FIGURE 2. Temperature dependence of the magnetic susceptibility, χ , in a field of 3 Oe on zero-field cooling (ZFC) and on field cooling (FC) for the single-crystal $\text{La}_{1.80}\text{Ba}_{0.07}\text{Sr}_{0.19}\text{Ca}_{0.97}\text{Cu}_{1.97}\text{O}_6$. The inset shows the temperature dependence of the in-plane electrical resistivity, ρ_{ab} .

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